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EFFECTS OF ANTIMONY SUBSTITUTION ON BISMUTH BASED SUPERCONDUCTORS

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Introduction

The discovery of high temperature superconductors of the LaBaCuO(1) and YBaCuO(2) families and the homologous series BiSrCaCuO(3-6) and TlBaCaCuO(7) has produced an explosion of interest, stimulating a great activity in the investigation of these new materials.

BiSrCuO was the first superconducting material that did not contain rare earth elements and has a critical temperature of about 20 K. The compound $Bi_2Sr_2CuO_6$ (2:2:0:1) in the standard notation was the first member of the family where double BiO rock salt-like layers alternate with CuO_2 sheets.

The other compounds of the bismuth family , with Ca addition, $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2) and $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2:2:2:3) are also built from double Bi-O layers with transition temperatures over 80 K for the low phase (L) and 110 K for the high phase (H). However, zero-resistance temperatures greater than 100 K are difficult to obtain in the 2:2:2:3 unless Pb(8) is added to the system.

Many attempts to enhance the transition temperature and improve the stability of the lattice have been made. Total and partial substitution, doping, and new compounds are constantly being reported.

A few papers have reported the existence of critical temperatures as high as 132 K(9) in the Bi based compound doped with Sb, and 140 K(10) by simultaneous chemical substitution of Sb and Pb. They claim that lead leads to a more stable and reproducible system. On the other hand other researchers(11,12) have found that Sb doping proved to be detrimental for the superconducting properties.

The work reported here was undertaken to investigate the effect of Sb substitution and simultaneous substitution of Pb and Sb on the superconducting transition temperatures in the BiSrCaCuO system; particularly in the 2:2:2:3 phase since any small increase in the transition temperature could be of great interest.

Experimental

More than 90 different samples were prepared based on 2:2:2:3 stoichiometry in the BiSrCaCuO system. After this preliminary attempt, four different families of samples have been investigated in the present study. In the first family of samples we substituted Bi by Sb to form $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_y$. The second group of samples were prepared by simultaneous addition of Pb and

Sb with nominal composition $Bi_{1.8}Pb_{0.1}Sb_{0.1}Sr_2Ca_2Cu_3O_y$. The third and fourth groups were prepared to determine the effect when the Pb concentration is increased; having nominal composition $Bi_{1.7}Pb_{0.2}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ and $Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3Oy$

High purity (99.99% - 99.999%) Bi_2O_3, PbO, Sb_2O_3, $SrCO_3$, CaO and CuO powders were weighed in different molar ratios. The weighed powders were dispersed in isopropyl alcohol, ball milled, dried and ground. The powder mixtures were calcined in air at 810°C for 20 hours, then reground and cold pressed into pellets (2 mm thick, 12 mm diameter), using 3000 psi pressure. The pellet samples were subsequently sintered in air with varying processing temperatures and times. The samples were not very sensitive to the cooling rate, so they were furnace cooled.

Samples were prepared in a Fisher furnace. The furnace had three ramp rates and their corresponding holding times, for both, heating and cooling. The temperature can be controlled up to 0.01 degree. The XRD scans were recorded using a Rigaku diffractometer with graphite monochomated CuKα radiation and Bragg-Brentano geometry.

DC temperature dependence resistivity measurements were carried out by the four probe standard technique using a closed cycle refrigerator system, with excitation current of 1 mA. The sample dimension was 0.21 cm(W), 0.15 cm(H) and 1.00 cm(L) Inductance measurement also were carried out, having the superconducting sample as a core in a small coil using a 4275A Hewlett Packard inductance meter.

Results and Discussion

Peaks for XRD at 5.72° and 4.78° (2θ values) corresponding to (200) reflections identify the low and high temperature phases, respectively. Unfortunately, those peaks are not very well defined in our spectra, therefore we concentrated our attention on the 2θ values of 23° (L) and 24° (H) which correspond to (008) and (0010) reflections respectively.

The first family of samples with stoichiometry $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ was heat treated in the temperature range from 810 °C to 900 °C. The most significant ones were sintered for 12 h at 873 °C and 878 °C after a previous calcination and additional sintering at 850 °C for 12 h. At 873 °C a small shoulder in the right side of the low temperature phase (23°) indicates the presence of a small amount of the high temperature phase. When the heat treatment temperature was increased to 878 °C, it produced signicant increases in the amount of the high temperature phase. However, when the processing temperature is increased further, the sample decomposes and the XRD pattern becomes very complicated. The 2:2:1:2 phase can still be identified.

The second set of samples were prepared in parallel conditions as the previous set. Figure 2, shows XRD data for the Sb/Pb compound with nominal composition $Bi_{1.8}Pb_{0.1}Sr_{0.1}Sr_2Ca_2Cu_3O_y$. They were sintered for 12 h at 868 °C, 873 °C, 878 °C, and 883 °C. As the sintering temperature increases from 868 °C to 878 °C the concentration of the low temperature phase seems to decrease in favor of the high temperature phase. Again increasing the processing temperature leads to the degradation of the high temperature phase and the system reenters to the 80 K phase. This behavior has been reported by many researchers in Bi based compounds containing Pb.

It must be mentioned that the x-ray diffraction peak corresponding to the high temperature phase starts to form at 850 °C but it has a very low intensity (I_H/I_L is aproximately 1/10). The temperature is higher for the samples with pure Sb.

The other two groups with 10% and 15% Pb substitution and 5% Sb present esentially the same behavior as the one described above. However, the Pb content tends to decrease the sintering temperature for the formation of the high temperature phase. Illustration of such behavior for our best samples of each group is given in figure 3.

Samples of the third and fourth families were treated for a very short time, 1 to 5 minutes, at temperatures between 880 °C to 930 C. The XRD patterns for this samples are depicted in figure 4. Samples with 10% Pb and 5% Sb, after the calcination process, were heated at 880 °C for 5 minutes and quenched in air. The result is a 2:2:1:2 phase highly oriented. When the sample is heated at 930 °C for 3 minutes the result is also a very highly oriented sample but the low temperature phase decomposes giving rise to the formation of 2:2:0:1 phase. This phase has a critical temperature at 20 K corresponding to the 20 value of 7.18°. The low temperature phase peak is not present any more.

Similar resuls were observed for samples with 15% lead concentration but the orientation effect seems to appear at slightly lower temperatures.

The electrical superconducting properties of the sample with 5% lead and 5% antimony are shown in figure 5. The resistivity of this sample exhibits metallic behavior in the normal state and starts to decrease sharply at about 115 K, with a second transition at 85 K and zero resistance at 40 K which is indication of a highly inhomogeneous superconductor.

Inductance measurements were taken showing clearly the presence of 2:2:1:2 and 2:2:2:3 phases.

Conclusions

According to our study we have found:

1) There is no evidence of temperature onset at 140 K or 132 K in samples with antimony and lead-antimony additions. On the contrary these substitutions leads invariably to a mixture of two superconducting phases, with the 85 K phase representing the major constituent.

2) Increase in lead doping promotes the formation of the 110 K phase at lower temperatures.

3) Increasing in sintering temperatures, after the formation of the high temperature phase, forces the system to reenter the low temperature phase.

4) Sintering temperatures very close to the melting point for a short periods of time produce very highly oriented samples in the 85 K phase. However, for temperatures much higher than the melting point, the orientation persist but the low temperature phase degrades, forming the very low temperature phase (20 K). As the lead concentration increases the orientation effect starts at lower temperatures.

5) The fact that small changes in sintering temperatures have a great impact on the phase transformation, maybe an indication that these transformations are characterized by very short diffusion path lenghts.

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Figure Captions

Fig 1. X-ray diffraction scan for $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ samples sintered for 12 h at (a) 873 °C and (b) 878 °C.

Fig 2. X-ray diffraction scan for $Bi_{1.8}Pb_{0.1}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ samples sintered for 12 h at (a) 868 °C, (b) 873 °C, (c) 878 °C, and (d) 883 °C.

Fig 3. X-ray diffraction data for (a) $Bi_{1.7}Pb_{0.2}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ sintered at 870 °C for 24 h, and (b) $Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ sintered at 860 for 60 h.

Fig 4. X-ray diffraction data for $Bi_{1.7}Pb_{0.2}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ sintered at (a) 880 °C for 5 minutes, and (b) 930 °C for 3 minutes.

Fig 5. Resistance temperature dependence curve for $Bi_{1.8}Pb_{0.1}Sb_{0.1}Sr_2Ca_2Cu_3O_y$.

References

(1) J. G. Bednorz, and K. A. Muller, Z. Phys. B **64**, 189 (1986)

(2) M. K. Wu, J. R. Ashburn, C. J. Tong, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

(3) C. Michel, M. Herview, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

(4) H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Japan. J. Appl. Phys. Lett. **27**, 2 (1988)

(5) P. Border, J. J. Capponi, C. Chaillout, J. Chenavas, A. W. Hewat, E. A. Hewat, J. L. Hodeau, M. Marezio, J. L. Tolence, and D. Tranqui, Physica C. **153-155**, 623 (1988).

(6) J. M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Huang, Phys. Rev. B **37**, 9382 (1988).

(7) Z. Z. Sheng, and A. M. Herman, Nature. **332**, 138 (1988).

(8) M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Tommi, and H. Mazaki, Jpn. J. Appl. **27**, L996 (1988).

(9) L. Hongbao, C. Liezhao, Z. Ling, M. Zhiqiang, L. Xiaoxian, Y. Zhidong, X. Bai, M. Xianglei, Z. Guien, R. Yaozhong, C. Zhaojia, and Z. Yuheng, Solid State Commun. **69**, 867 (1989).

(10) C. Tingzhu, L. Jiang. F. Chengao, Y. Li, L. Yuntao, Z. Guien, M. Zhiqiang, W. Haiqian, C. Zhaojia, and Z. Yuheng, Supercond. Sci. Technol. **3**, 87 (1990).

(11) P. K. Ummat, W. R. Datars, V. V. Gridin, and C. V. Stagar, Solid State Commun. **74**, 983 (1990).

(12) C. V. Tomy, R. Prasad, N. C. Soni, K. Adhikary, A. Guinar, and S. K. Malik, Solid State Commun. **74**, 493 (1990).

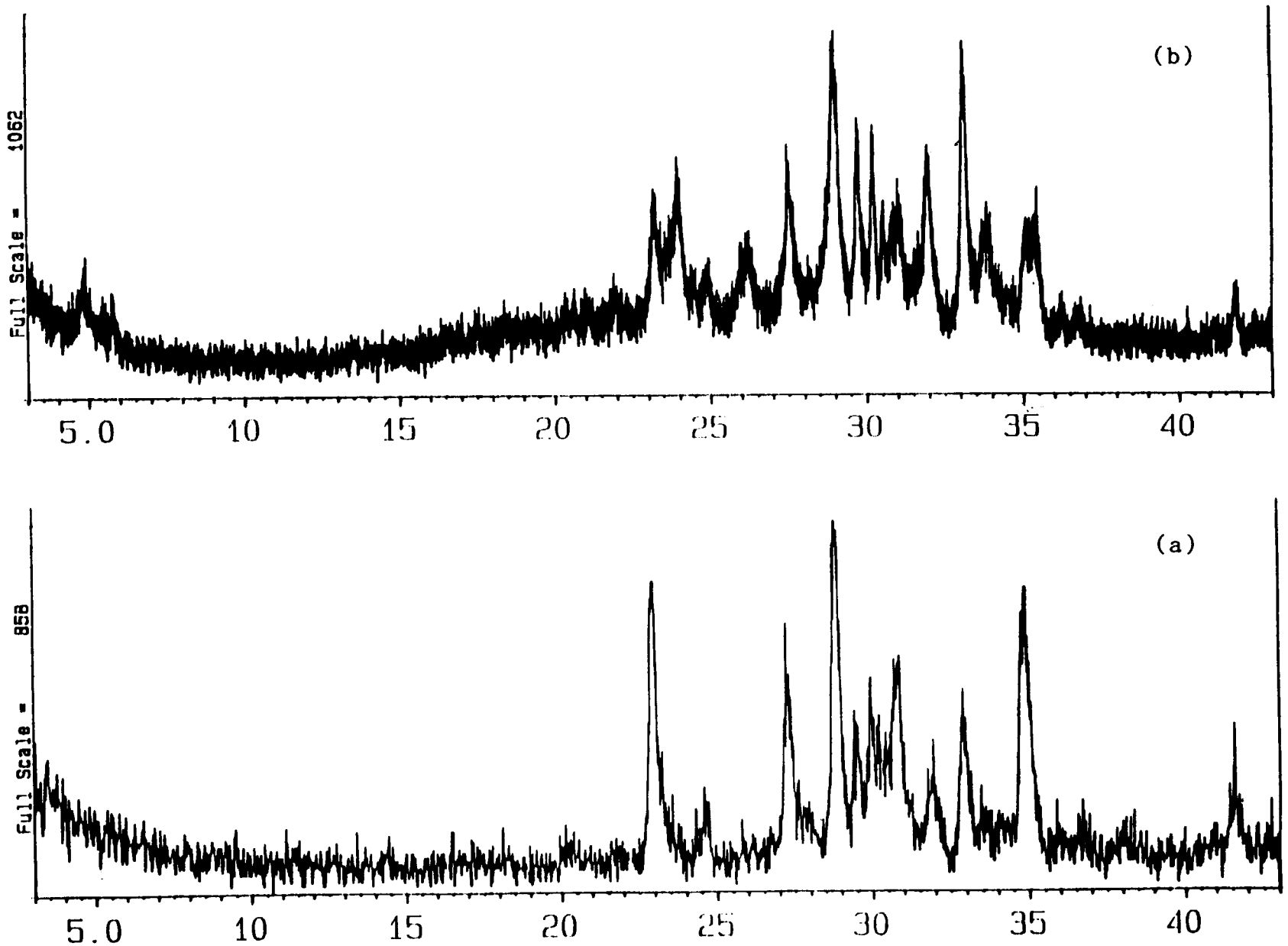
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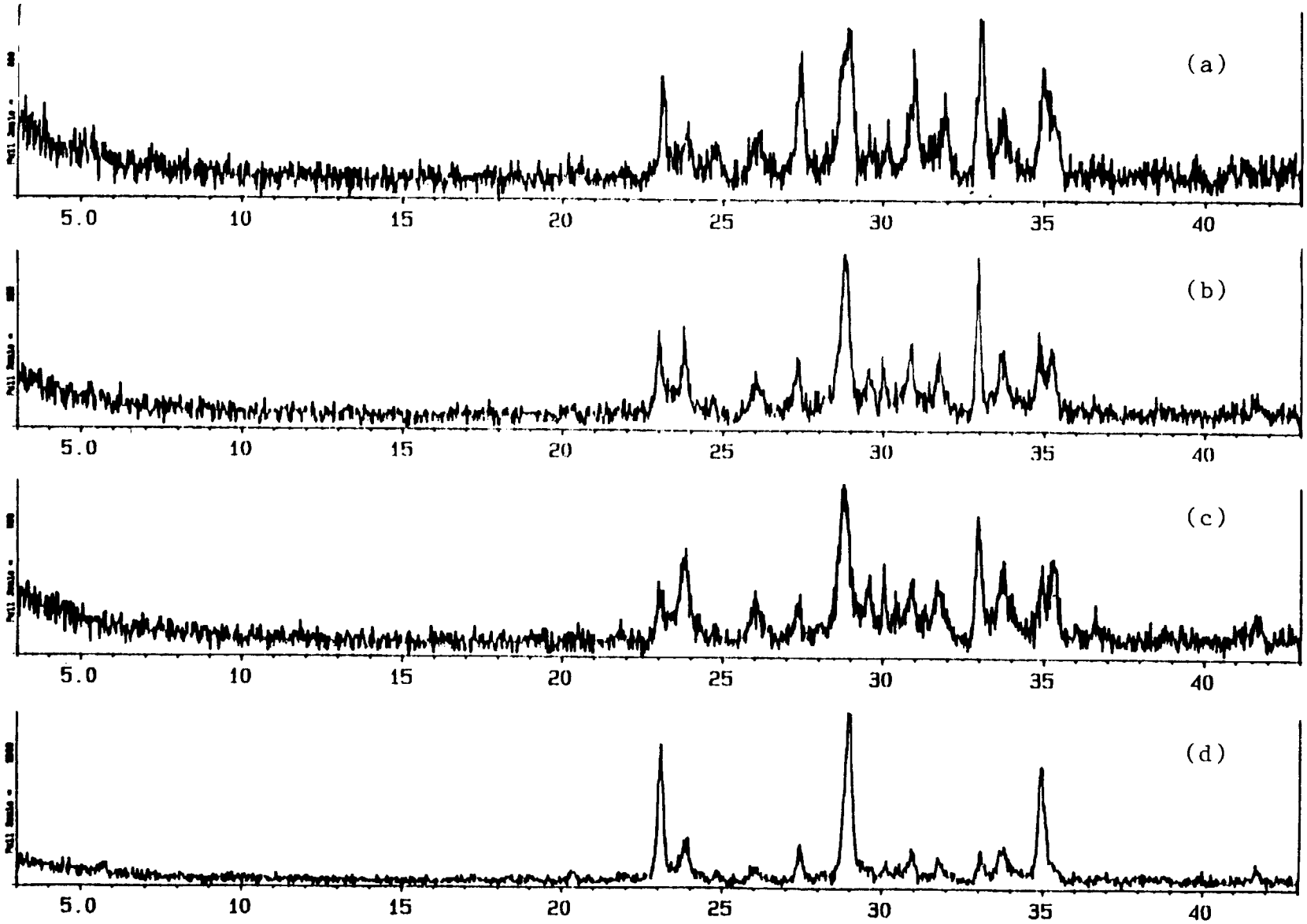
Figure 1.



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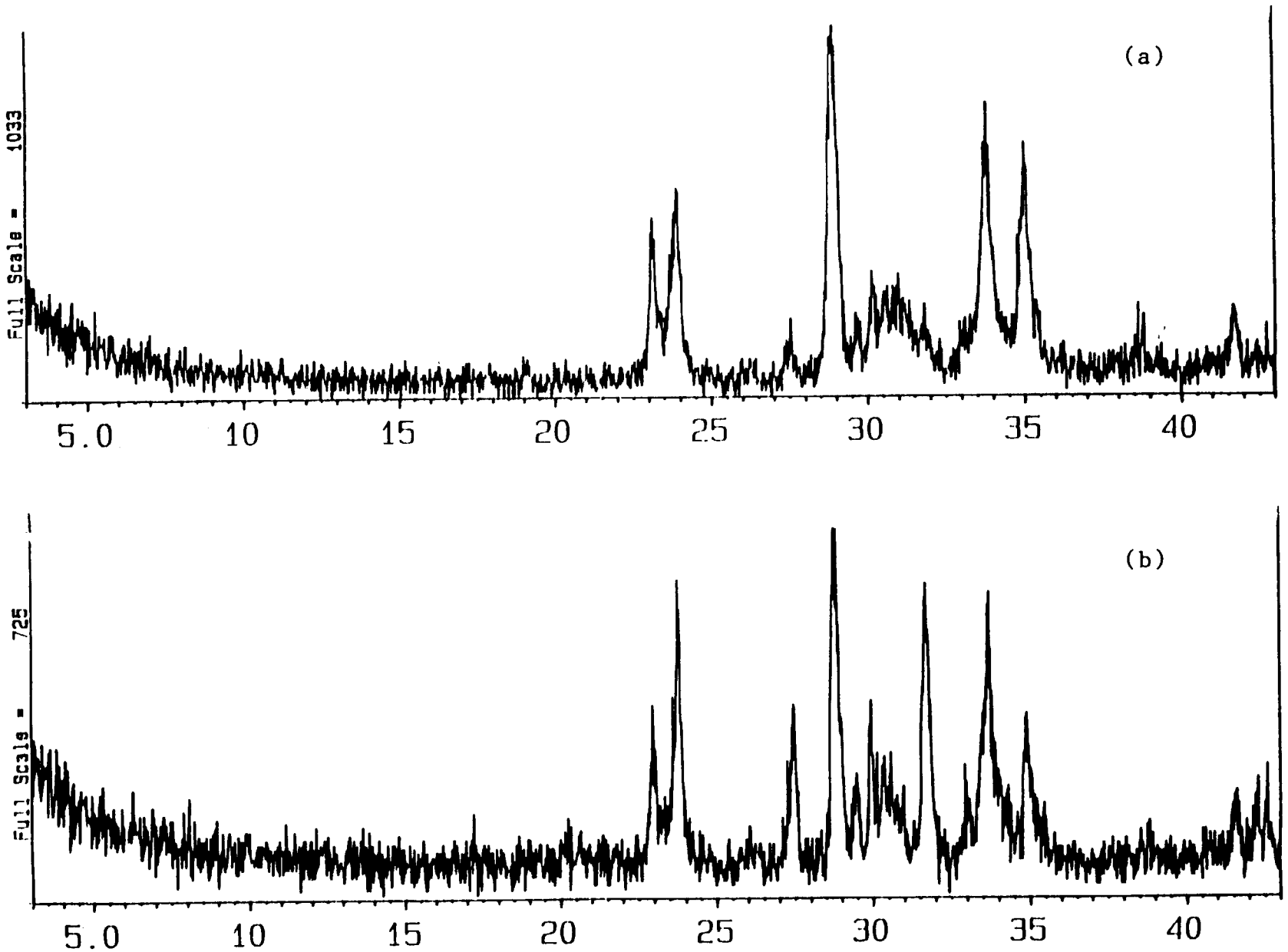
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Figure 3.

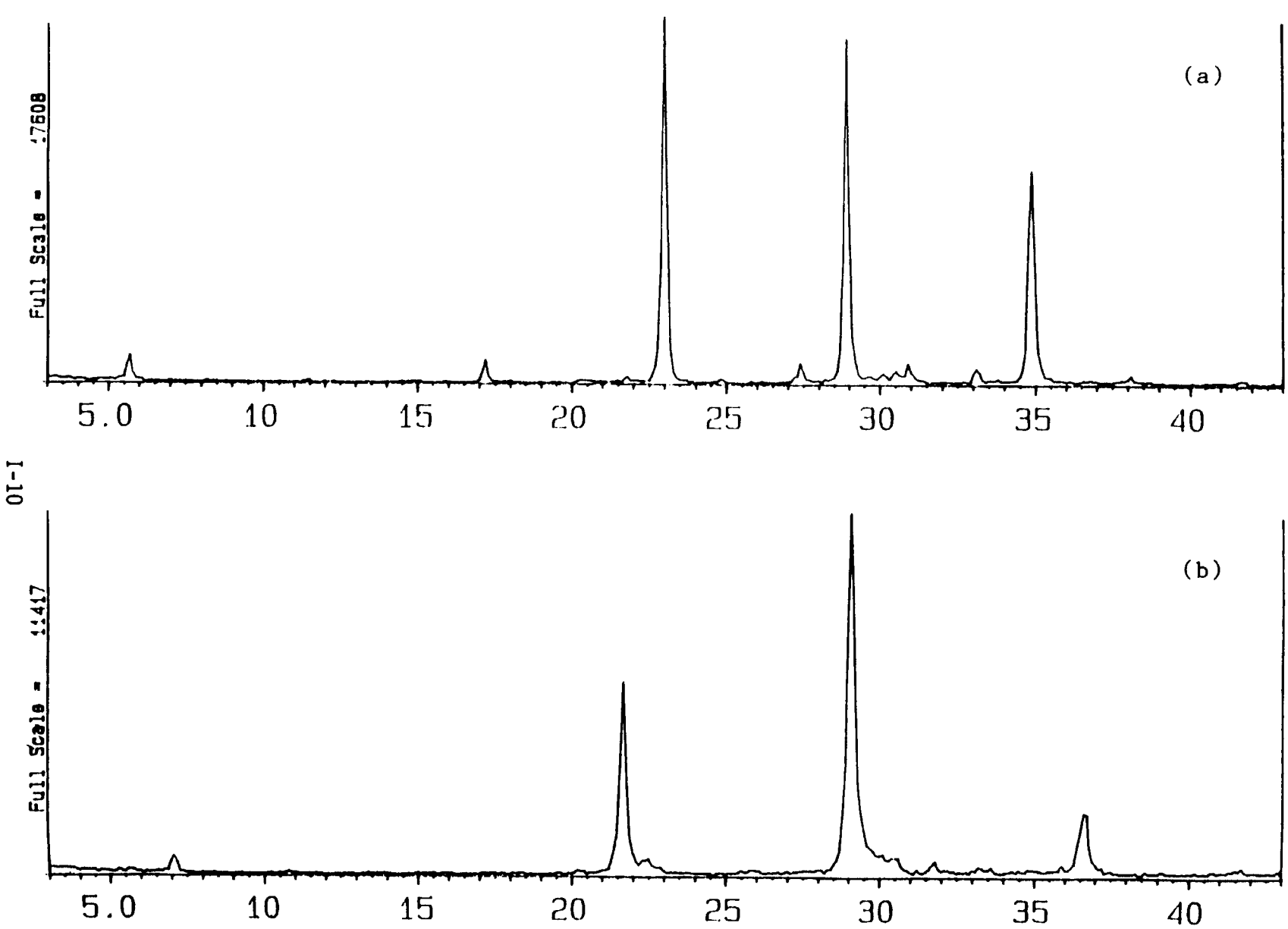
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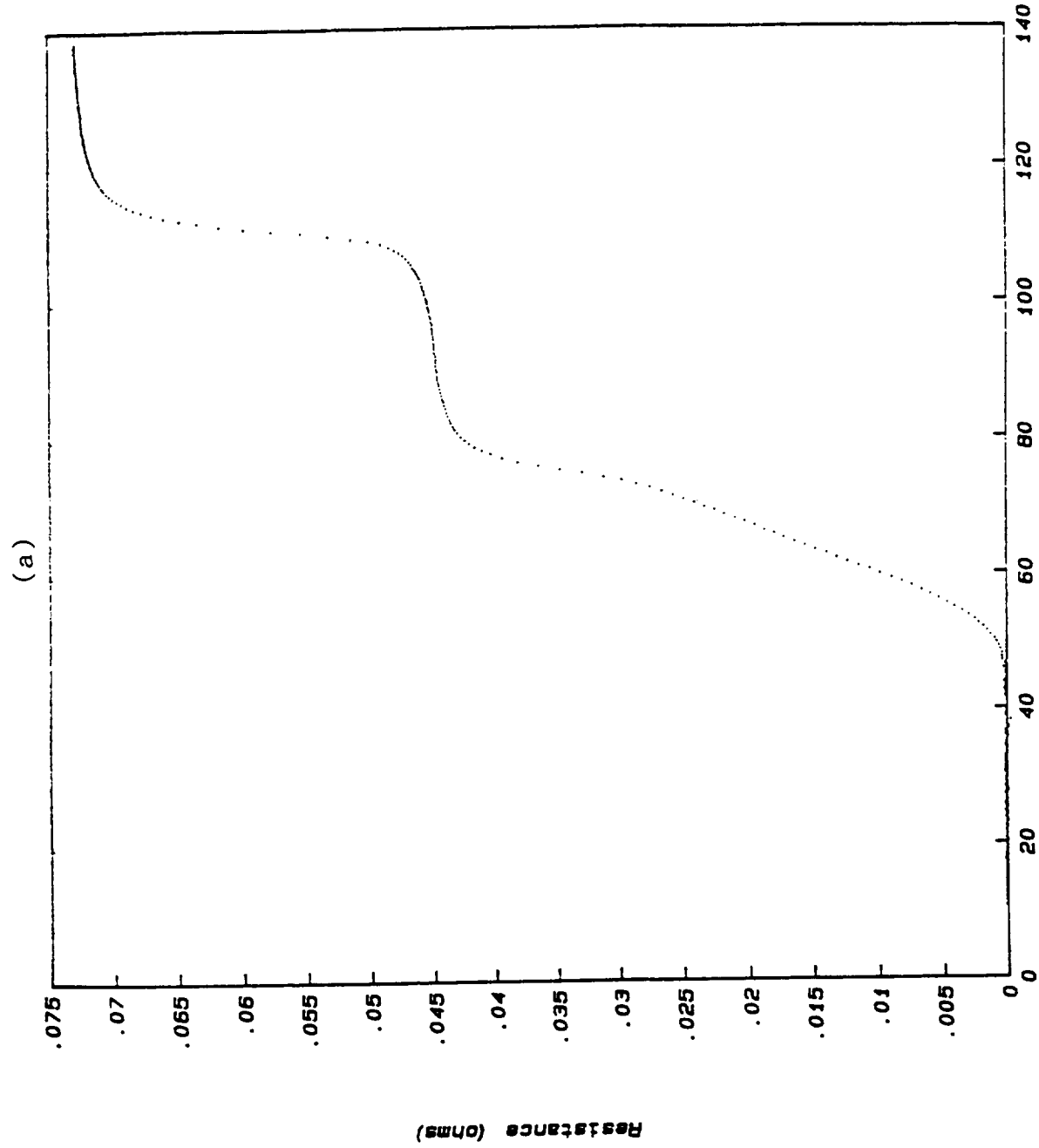
Figure 4.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Resistance (ohms)
0
20
40
60
80
100
120
140
Temperature (K)

Figure 5.